Holz als Roh- und Werkstoff 61 (2003) 221–226 © Springer-Verlag 2003
DOI 10.1007/s00107-003-0389-2

Color stability of heat-treated wood during artificial weathering

N. Ayadi, F. Lejeune, F. Charrier, B. Charrier, A. Merlin

Abstract The color change of wood after exposure to UV light may produce aesthetical damages. The stability of the color to light exposure is an important issue. This study describes experiments of testing the color stability of heat-treated wood samples. Heat treatment was done at 240 °C during 2 hours, under nitrogen. Heat-treated samples of ash, beech, maritime pine and poplar heartwood were exposed to UV-light (QUV equipped with fluorescent lamps UVA-340) during 835 hours. Color measurements during accelerated weathering were made at intervals throughout the test period. The results are presented in ΔE and L^* a^* b^* coordinates according to the CIELab system. The experiments show that the color stability for heat-treated wood is better during the 835 hours of exposure when compared to untreated wood. The properties of heat treated wood (lignin modifications, and monomers of phenolic compounds) are probably involved in the retified wood resistance against UV light under experimental conditions.

Farbstabilität von hitzebehandeltem Holz während künstlicher Bewitterung

Zusammenfassung Farbveränderung bei Holz, das UV-Licht ausgesetzt wurde, kann ästhetische Schäden verursachen. Die Stabilität der dem Licht ausgesetzten Farbe ist ein wichtiges Thema. Diese Studie beschreibt Experimente zum Testen der Farbstabilität bei hitzebehandelten Holzproben. Die Hitzebehandlung wurde bei 240 °C zwei Stunden lang unter Stickstoff durchgeführt. Die hitzebehandelten Holzproben von Eschen-, Buchen-, Kiefern- und Pappel-Kernholz wurden 835 Stunden lang UV-Licht ausgesetzt (QUV bestückt mit fluoreszierenden Lampen UVA-340). Farbmessungen während beschleunigter Bewitterung wurden in Intervallen durchgeführt. Die Ergebnisse werden in ΔE und L^* a^* b^* Koordinaten gemäß dem CIELab-System dargestellt. Sie zeigen, dass die Farbstabilität bei hitzebehandeltem Holz während der 835 Stunden vergleichsweise besser ist als bei unbehandeltem Holz. Die Eigenschaften des hitzebehandelten Holzes (Ligninmodifikationen und monomere phenolische Bestandteile) sind wahrscheinlich an der Beständigkeit gegenüber UV-Licht unter experimentellen Bedingungen beteiligt.

1
Introduction

Exposed to solar irradiation, wood changes color. Some woods become bleached or grey, others turn yellow, red-orange or brown colors depending on the influence of the wood compositions (especially extractive compositions) (Sandermann et al. 1962).

Among all environmental factors, UV light is one of the most effective parameter in contributing to the weathering of wood (Kalnins 1966; Futo 1974; Feist and Hon 1984). Wood is capable of absorbing all wavelengths of electromagnetic radiation (UV-light penetrates approximately 75 μm and visible light approximately 200 μm) to initiate photochemical reactions that may ultimately lead to wood discoloration and photodegradation (Hon 1981). According to Norrstrom (1969), lignin contributes 80–95%, carbohydrates 5–20%, and extractives about 2% to the total UV absorption coefficient of wood. Lignin has an absorption peak at 280 nm, with its tail extending to 400 nm in the visible region (Hon 1981).

The light induced degradation of wood is considered mainly due to the photochemical reactions occurring in lignin. α-carbonyl, biphenyl and ring-conjugated double bond structures in lignin can absorb UV-light and form chromophores (Lin et al. 1970). The degradation occurs through radical reactions. The absorption of light by the chromophoric groups of lignin leads to the formation of radical species with long life time. These free radicals react with oxygen to produce chromophoric groups as carbonyl and carboxyl groups (Hon 1991). These structures are responsible for the wood color changes (Dirckx et al. 1987).

Oxygen plays a part in the photodegradation process. Water is also considered to be a critical element in wood's photodegradability. It has been suggested that the principal role of water is to facilitate light penetration into the accessible regions and to open non accessible region for light penetration (Hon 1973).

Published online: 7 May 2003

N. Ayadi, F. Lejeune
Ecole Supérieure du Bois,
rue Christian Pauc,
44 306, Nantes Cedex 03, France

F. Charrier, B. Charrier (✉)
Département Science et Génie des Matériaux orientation bois,
Université de Pau et des Pays de l'Adour,
40 004 Mont de Marsan, France
E-mail: bertrand.charrier@univ-pau.fr

A. Merlin
LERMAB, Université Henri Poincaré,
54 500 Vandoeuvre les Nancy, France

To limit wood photodegradation, many chemical protections were investigated: blocking of the phenolic groups and reduction of carbonyls. Acetylation inhibits wood yellowing, but causes lightening of wood during its exposure to the solar radiation. The yellowing of the fir wood (Abies grandis) impregnated by a solution of hydroxybenzophenone and hydroxybenzotriazole UV lights are not completely inhibited. The grafting of UV absorbers improves the durability of protection (Williams 1983). The hydroxy amino light stabilizers (HALS), which are often used for the stabilization of synthetic polymers, accelerate the yellowing of fir wood (*Abies grandis*). Treatments with inorganic salts can protect wood from photodegradation. The best performances are observed with chromium salts by Feist and Hillis in 1978, but color modification induced by the treatment and the toxicity of chromium limit its application.

For decorative end-use (parquets, panels, furniture, etc.), and exterior joinery protected by clear coatings, the color stabilization of natural wood surface is required. The finding of new treatments stabilizing wood surface color, would easily find applications in industry (i.e. joinery for example). Recently, some companies in Germany, Switzerland and, also in France have been working on some new Generation UV absorbers which appear to work more efficiently.

The torrefaction of wood is its treatment at high temperature. For fifteen years, some European researchers have studied retification process to improve wood quality (Gohar and Guyonnet 1998). Such treatment at high temperature of 240 °C and under inert atmosphere permits to improve toughness and, in some ways, wood resistance against fungi (Kamdem et al. 2002). Although it darkens the color of wood, it was shown that this treatment can improve physicochemical and biochemical properties of the material such as reduction of hydroscopicity, increase of dimensional stability and resistance against biological degradation (Avat 1993). These properties allow use of retified wood in environmental hard classes 3 (EN 350). The color change caused by treatment can sometimes be well appreciated by customers (This is especially the case with the woods like poplar, ash, pine and beech which have clear colors).

2
Material and methods

2.1
Test specimens and heat treatment

In this paper we have studied four wood species samples: ash (*Fraxinus* sp), beech (*Fagus sylvatica* L.), maritime pine (*Pinus pinaster*) and poplar (*Populus sp.*). Each species was exposed to UV light. For each species six heartwood samples of 150 × 75 × 5 mm (longitudinal by radial by tangential) were provided. Four samples were treated at 240 °C under anaerobic atmosphere in Retitech Society (located in Chambon in France) and two samples were used as references.

2.2
Weathering tests

Accelerated weathering test was conducted in a Q-panel QUV weathering tester (Q-panel company, USA) equipped with UVA-340 lamps. Four heat-treated samples and two untreated control samples of each species, were exposed to UV light directly at a distance of 5 cm for 835 hours. Each cycle comprised 2h30 of irradiation at 60 °C followed by 30 min of condensation at 50 °C.

2.3
Color measurement

The color of the samples was measured every 24 hours during the first 7 days, then once a week until the end of the weathering test. The measurements were done with a MICROFLASH 200d spectrocolorimeter, equipped with an integrating sphere. The CIE Lab system is characterized by three parameters, L^*, a^* and b^* (Fig. 1). L^* axis represents the lightness, it varies from 100 (white) to zero (black), a^* and b^* are the chromaticity coordinates. In the diagram CIELAB, $+a^*$ is the red direction, $-a^*$ is green, $+b^*$ is yellow, $-b^*$ is blue. Before and after the weathering test, L^*, a^* and b^* color coordinates of each sample were calculated based on a D65 light source by simulating the daylight. These values were used to calculate the color change ΔE^* as a function of the weathering time according to the following equations:

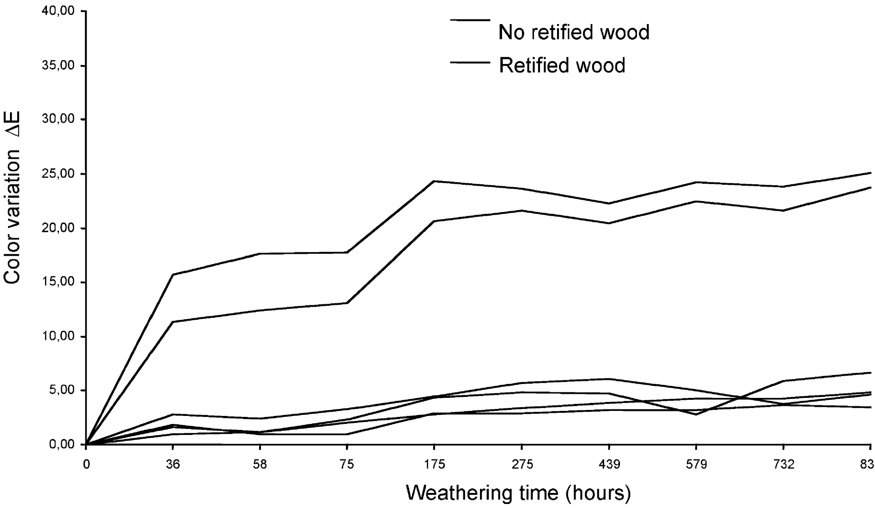


Fig. 1. Color change of heat-treated (retified) and untreated (no retified) ash samples during accelerated weathering with QUV (835 hours according a cycle of 2h30 UV-irradiation and 30 min condensation). Each value is a mean of three measurements and each curve is corresponding to one wood sample (four heat treated and two no treated)

Abb. 1. Farbveränderung hitzebehandelter und -unbehandelter Eschenproben mit QUV (835 Stunden lang gemäß einem zweieinhalbstündigen Zyklus UV-Strahlung und 30-minütiger Kondensation) während beschleunigter Bewitterung. Jeder Wert ist ein Mittel dreier Messungen und jede Kurve entspricht jeweils einer Holzprobe (vier hitzebehandelt und zwei unbehandelt)

$$\Delta L_t* = L_t* - L_i*$$
$$\Delta a_t* = a_t* - a_i*$$
$$\Delta b_t* = b_t* - b_i*$$
$$\Delta E_t* = \left[(\Delta L_t*)^2 + (\Delta a_t*)^2 + (\Delta b_t*)^2\right]^{1/2}$$

where, ΔL_t^*, Δa_t^*, and Δb_t^* are the color coordinate change.

2.4
Chemical analysis

2.4.1
Extraction

Extraction was carried out with a Dionex extractor monitored by the extracting system ASE (r) 200. After leaching with petrol ether for 24 hours, sawdust was extracted with a solution of ethanol-water (70:30) at a temperature of 100 °C, and pressure of 100 bar in 2 cycles. The static time was 5 min.

2.4.2
Total phenol contents

Total phenol contents was determined by the Folin-Ciocalteu method (Singleton and Rossi 1965). 2.5 ml of Folin-Ciocalteu reagent and 2 ml of aqueous solution of sodium carbonate (75 g/l) are added to 0.5 ml of the extract diluted by water. The mixture was exposed to 50 °C for 5 min, and, after cooling absorbance was measured at 760 nm. Aqueous solutions of gallic acid (20–80 PPm) were used as standards.

2.4.3
Polysaccharides contents

Polysaccharides contents was determined by the Dubois method (Dubois et al. 1956). 1 ml of the extract was mixed with 1 ml of phenol (5%) and 5 ml of concentrated sulfuric acid (98%). The mixture was maintained 20 min at 25 °C. Absorbance was measured at 490 nm. Calibration was achieved with aqueous solutions of glucose (20–80 PPm).

3
Results

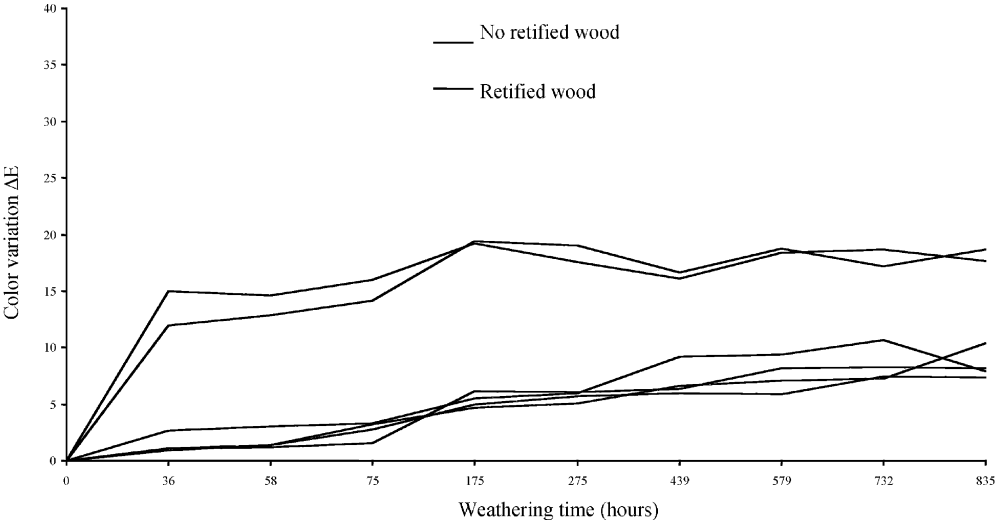
3.1
Color changes

The color stability of the four material classes, untreated and heat-treated, was examined by means of the amount of the color difference ΔE (Fig. 1, 2, 3 and 4). Like it was already observed on pine douglas fir and red cedar after outdoor experiments, (Kleinert 1970), the samples tested showed quick changes during the first 36 hours of exposure. Especially on untreated materials we have observed a strong color change during the first 36 hours compared to the treated ones. The treated materials changed little throughout the 835-hour exposure. During the first irradiation step, we observed a quick darkening, yellowing and reddening of non retified wood. These color modifications were softened in the case of treated wood. However, in Fig. 3 (poplar samples) we have observed a different behavior on one of the treated wood samples whose kinetic was similar to the non-treated woods during the first 36 hours of treatment. After this period of treatment, color change was intermediate between retified wood and non-retified wood at the beginning of the treatment and artificial weathering.

Final color changes at the end of the 835-hour treatment were clearly much greater for the non-treated wood than the treated ones. For all species the final color changes in 835 hours were clearly stronger for the untreated wood than the treated ones. In Fig. 5 we observe strong differences: Delta E

Fig. 2. Color change of heat-treated (retified) and untreated (no retified) beech samples during accelerated weathering with QUV (835 hours according a cycle of 2h30 UV-irradiation and 30 min condensation). Each value is a mean of three measurements and each curve is corresponding to one wood sample (four heat treated and two no treated)

Abb. 2. Farbveränderung hitzebehandelter und unbehandelter Buchenproben mit QUV (835 Stunden lang gemäß einem zweieinhalbstündigen Zyklus UV-Strahlung und 30-minütiger Kondensation) während beschleunigter Bewitterung. Jeder Wert ist ein Mittel dreier Messungen und jede Kurve entspricht jeweils einer Holzprobe (vier hitzebehandelt und zwei unbehandelt)



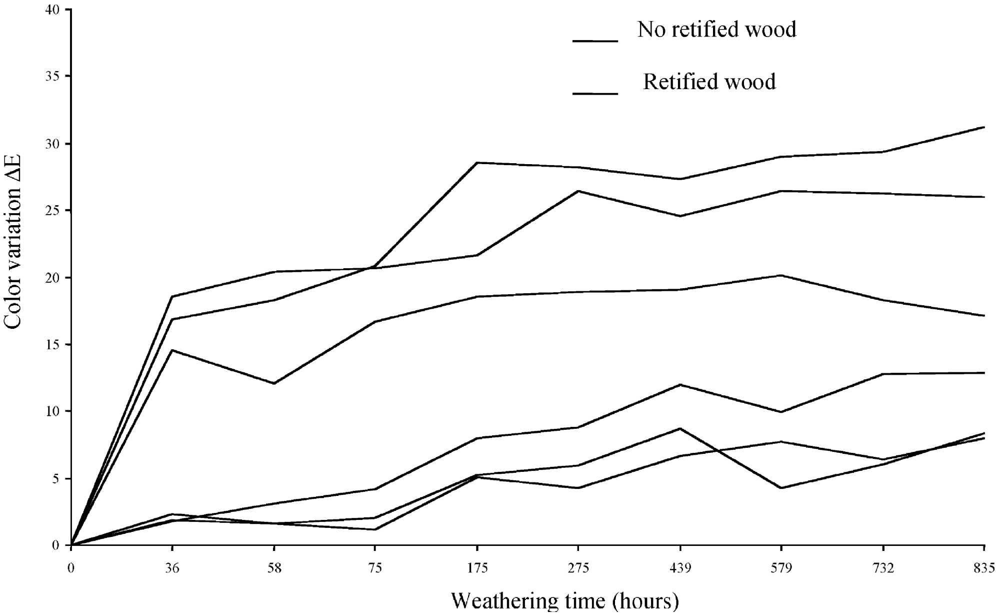


Fig. 3. Color change of heat-treated (retified) and untreated (no retified) poplar samples during accelerated weathering with QUV (835 hours according a cycle of 2h30 UV-irradiation and 30 min condensation) Each value is a mean of three measurements and each curve is corresponding to one wood sample (four heat treated and two no treated)

Abb. 3. Farbveränderung hitzebehandelter und unbehandelter Pappelproben mit QUV (835 Stunden lang gemäß einem zweieinhalbstündigen Zyklus UV-Strahlung und 30-minütiger Kondensation) während beschleunigter Bewitterung. Jeder Wert ist ein Mittel dreier Messungen und jede Kurve entspricht jeweils einer Holzprobe (vier hitzebehandelt und zwei unbehandelt)

is two times more important for beech and poplar, 3 times for pine and 5 times for ash, in non treated wood.

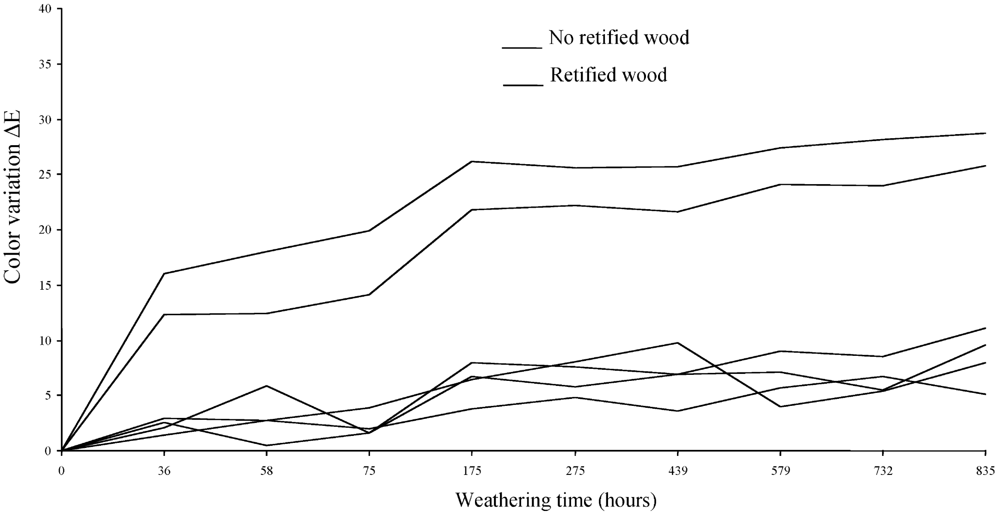
3.2
Chemical analysis

Total phenols and sugar were quantified before and after retification for ash, beech and poplar species. Fig. 6 shows that, after wood treatment phenol contents of all materials increase. As it is described in Fig. 7, sugar contents increase only in beech and poplar. This content increase could be explained by the degradation of chemical wood components, such as hemicelluloses, lignin and extractive compounds, during the heat treatment (Avat 1993).

pH measurements of the extracted solutions of retified and non-retified wood, indicate an increase of acid products during the heat treatment (Table 1). This increase appears to be more important for ash wood when we compare it with other species.

Fig. 4. Color change of heat-treated (retified) and untreated (no retified) maritime pine samples during accelerated weathering with QUV (835 hours according a cycle of 2h30 UV-irradiation and 30 min condensation). Each value is a mean of three measurements and each curve is corresponding to one wood sample (four heat treated and two no treated)

Abb. 4. Farbveränderung hitzebehandelter und unbehandelter Pinienproben mit QUV (835 Stunden lang gemäß einem zweieinhalbstündigen Zyklus UV-Strahlung und 30-minütiger Kondensation) während beschleunigter Bewitterung. Jeder Wert ist ein Mittel dreier Messungen und jede Kurve entspricht jeweils einer Holzprobe (vier hitzebehandelt und zwei unbehandelt)



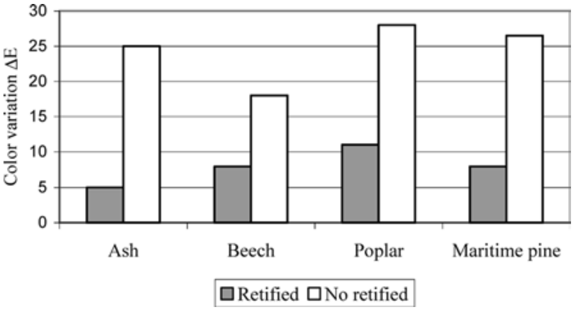


Fig. 5. Color variation (ΔE) of retified and no retified wood after 835 hours of artificial weathering. Each value of color variation is obtained by measurement of all the samples (four treated samples and two no treated samples)
Abb. 5. Farbunterschied (ΔE) von hitzebehandeltem und unbehandeltem Holz nach 835 Stunden künstlicher Bewitterung. Jeder Wert des Farbunterschieds wurde durch Messung aller Proben erhalten (vier hitzebehandelt und zwei unbehandelt)

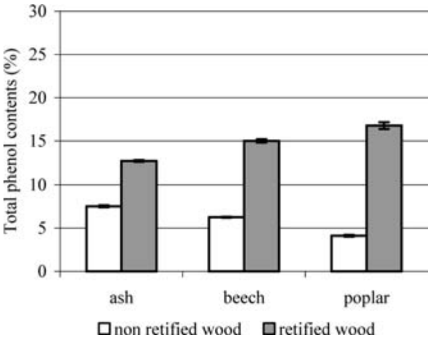


Fig. 6. Percentage of total phenols in the ash, beech and poplar wood before and after retification. Each value of retifiedwood is a mean of four analysis (one for each wood sample). For no retified wood two analysis have been done
Abb. 6. Anteil des Gesamtphenols in Esche, Buche und Pappel vor und nach Hitzebehandlung. Jeder Wert des hitzebehandelten Holzes ist ein Mittelwert von vier Analysen (eine für jede Holzprobe). Für unbehandeltes Holz wurden zwei Analysen ausgewertet

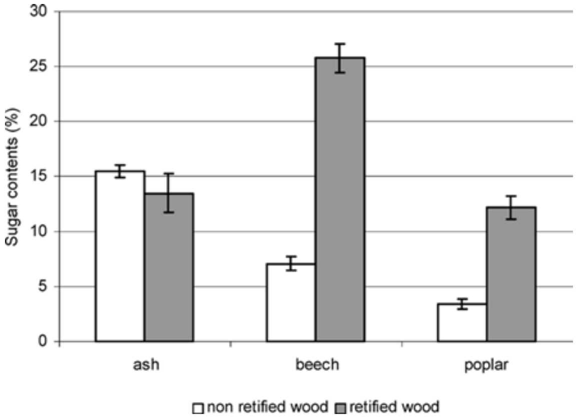


Fig. 7. Percentage of sugar in the ash, beech and poplar wood before and after retification. Each value of retified wood is a mean of four analysis (one for each wood sample). For no retified wood two analysis have been done
Abb. 7. Anteil des Zuckers in Esche, Buche und Pappel vor und nach Hitzebehandlung. Jeder Wert des hitzebehandelten Holzes ist ein Mittelwert von vier Analysen (eine für jede Holzprobe). Für unbehandeltes Holz wurden zwei Analysen ausgewertet

4
Discussion

We have shown that the heat treatment increases wood color stability, phenol, sugar and acid product contents. It was demonstrated that wood photodiscoloration is mainly due to lignin photodegradation (Dirckx 1988; Dirckx et al. 1992), and that extractives have antioxidant properties and can limit wood color change to light (Kalnins 1966, Mazet 1988). According to Kollman and Fengel 1965, heating at 175 °C caused a lignin condensation which increased with the heating temperature up to 240 °C. Therefore, the best photostability of retified wood color could be partially explained by the increase of lignin stability by condensation, and phenol content during the heat treatment.

Chemical analysis of wood after thermal treatment at high temperature shows a degradation of cellulose, hemicelluloses (Kollman, Fengel 1965) and extractives (Avat 1993). Sandermann and Augustin (1963) studied the thermal degradation of polyoses, and found that monosaccharides are produced during the cleavage of polysaccharidic chains, and that the final production of thermal degradation are methanol, acetic acid and volatile heterocyclic compounds (furan, γ-valerolactone). The improvement of acidity after the heat treatment observed on our samples may be explained as the production of acids coming from sugar degradation. By raising the temperature above 200 °C the thermal degradation of cellulose proceeds rapidly and generates monosaccharides as anhydroglucoses, furan and furan derivatives (Shafizadeh, DeGroot 1976). According to these results, we can think that the increase of sugar content in retified woods is mainly due to the degradation of hemicellulose and cellulose, and that the production of acid compounds is the result of polyoses degradation. Ash wood presents no change either in sugar quantities or in larger acidity after retification. We can suppose that the pathway of cellulose thermal degradation in ash wood is different from other species and that generated monosaccharides which are less resistant to high temperature, continue to degrade into acid products.

5
Conclusion

Retified wood behavior to UV light differs from untreated wood. We observed that if the heat treatment confers a

Table 1. pH of wood of different species, before and after heat treatment. Each value is a mean of 4 analysis on 4 wood samples
Tabelle 1. pH-Wert verschiedener Holzarten vor und nach Hitzebehandlung. Jeder Wert ist ein Mittelwert von 4 Analysen bei 4 Holzproben

Species	No retified wood		Retified wood	
	mean	Stdv	mean	stdv
Ash	5.5	0.3	4.8	0.2
Beech	5.3	0.4	5	0.1
Poplar	5.8	0.2	5.4	0.2

browning on wood, it also turns the surface of wood less sensitive to the phenomena of reddening and yellowing on untreated wood. The better resistance of retified wood to light can be attributed to the less attack of lignin. A part of this molecule changed during the heat treatment, and many monomers of phenol have been appeared. The explanation could be that the presence of antioxydant compounds after heating, can limit degradation caused by oxygen and radicals. In order to determine the components responsible for the behavior of retified wood more precisely, qualitative analysis should be carried out.

These observations will be useful for users of retified wood, who are in search of new finishing systems able to protect the surface of woods against UV light better than the existing ones.

References

Avat F (1993) Contribution à l'étude des traitements Thermiques du bois jusqu'à 300 °C: Transformations chimiques et caractérisations physico-chimiques—Thèse de l'Ecole Nationale des Mines de Paris et de l'Ecole Supérieure des Mines de Saint-Etienne, 240 p

Dirckx O, Masson D, Deglise X (1987) Actes du 2ème colloque Sciences et industries du bois. Nancy 22–24 Avril Tome II

Dirckx O (1988) Etude du comportement photochimique de l'Abies grandis sous irradiation solaire—Thèse de 3ieme cycle en sciences du bois, Université de NancyI

Dirckx O, Triboulot-Trouy MC, Merlin A, Deglise X (1992) Modifications de la couleur du bois d'Abies grandis exposé à la lumière solaire. Ann Sci For 49:425–447

Dubois M, Gilles KA, Hamilton JK, Rebers PA, Smith F (1956) Colorimetric method for determination of sugars and related substances. Anal Chem 28:350–356

Feist WC, Hon DNS (1984) Chemistry of weathering and protection—In: "The chemistry of Solid wood," R.M. Rowell, ed. Advances in chemistry series 207," Am. Chem. Soc., Washington D.C.

Feist WC, Hillis D (1978) Wood science 17(2):75–81

Futo LP (1974) Der photochemische Abbau des Holzes als Präparations- and Analusenmethode. Holz Roh- Werkstoff 32:303–311

Gohar P, Guyonnet R (1998) Development of wood retification, process at the industrial stage. Proceedings of the 4th Symposium International Wood Preservation. Cannes

Hon NS (1981) Photochemical degaradation of lignocellulosic materials. *In*: "Developments in Polymer degradation," N. Grassi, ed. Appl Sci Publ, London

Hon NS (1973) Formation of free radicals in photoirradiated cellulose and related compounds. Journal Polym Sci, Chem. Ed. 13:955

Hon NS (1991) Photochemistry of wood in wood and cellulosic chemistry. 525–555 pp

Kalnins MA (1966) Photochemical degradation of wood—In: "surface characteristics of wood as they affect durability of finishes," U.S. For. Serv., Res. Pap. FPl 57

Kalnins AM (1966) Surface characteristics of wood as they affect durability of finishes. Part II. Photochemical degradation of wood. US for Serv Rés Paper FPL 57:23–60

Kamdem DP, Pizzi A, Jermannaud A (2002) Originalarbeiten. Originals: Durability of heattreated wood. Holz Roh- Werkstoff 60(1):1–6

Kleinert TN (1970) Photochemical changes of wood surfaces in the open atmosphere, Holzforsch Holzverwert 22:21

Kollman F, Fengel D (1965) Holz Roh- Werkstoff 21:77–85

Lin SY, Kringstad KP (1970) Photosensitive groups in lignin and lignin model compounds, Tappi 53(4):658–663

Mazet JF (1988) Couleur et qualité des placages de chene et étude de leur comportement photochimique. Thesis in Wood Science, Nancy I University

Norrström H (1969) Light absorbing properties of pulp and paper components. Svensk Paperstidn 72:25–38

Sandermann W, Schlambom F (1962) On the effect of filtred ultraviolet light on wood—Part I and Part II. Holz Roh- Werkstoff 20:245, 285

Shafizadeh V, DeGroot WF (1976) Combustion Characteristics of cellulosic fuels. In: Thermal uses and properties of carbohydrates and lignins. Academic Press, New York, San Francisco, London, pp. 1–17

Singleto VL, Rossi JA (1965) Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. Am J Enol Vitic 16:144–158

Sundqvst B (1999) Colour stability of capillary phase heat-treated wood exposed to UV light—Proceedings of the Fourth International Conference on the Development of Wood Science, Wood Technology and Forestry, Missenden Abbey, UK, 14–16 July 1999. pp. 172–182, 12 ref.

William RS (1983) Effect of grafted UV stabilizers on wood surface erosion and clear coating performance. J Applied Polymer Science 28:2093–2103